SYNOPSIS OF

Synthesis and Characterization of Fe and Fe-Ni co-doped ZnO Diluted Magnetic Semiconductor

A THESIS

to be submitted by

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Introduction & Literature Review

Spintronics (“*spin transfer electronics’’)* is a new research field, which studies possible applications of both spin and charge of the electrons. Diluted magnetic semiconductors (DMS) are promising candidates for such applications. This class of materials has been discovered because of their property of exhibiting room temperature ferromagnetism or well above it, since they have the potential of being used in optoelectronic, magneto electronic or other devices using both spin and charge of the electrons. Two major criteria are considered to select the most promising materials for semiconductor spintronics. First, the ferromagnetism should be retained to practical temperatures namely room temperature. Second, it would be a major advantage if we can modify an already existing technology base for the material in other applications. Today’s research on spin electronics involves all material families, the most mature being studies on magnetic metal multilayers, in which spin-dependent scattering and tunneling are being successfully applied in reading heads of high density hard-discs and in magnetic random access memories (MRAM). However, in the context of spintronics particularly promising are ferromagnetic semiconductors since they combine the properties of ferromagnetic and semiconductor material systems. The first excellent surveys of the field of magnetic semiconductors were given by Methfessel as well as by Austing and Elwell in 1970 [1-2]. These types of materials provide a new type of control of conduction based on control of quantum spin state (up or down) and charge. These provide near total spin polarization theoretically opposite to iron or other metals which provide only ~ 50% polarization and is an important property for spintronic applications, e.g: spin transistors. So, Diluted Magnetic Semiconductors have been recently a major focus of magnetic semiconductors research. The family of diluted magnetic semiconductors implies those standard semiconductors, in which a sizable portion of atoms is

substituted in place of non-magnetic semiconductors host matrix by such elements which produce localized magnetic moments in the semiconductor. From the theoretical predictions transition metal doped ZnO has emerged as most promising DMS candidate for spintronics [3-4]. ZnO is a semiconductor material of II-VI compound whose ionicity lies at the borderline between covalent and ionic semiconductor. This characteristic leads to a repulsion of its electronic clouds of charge thereby causing that their electronic structure more stable is wurtzite.

ZnO-based diluted magnetic semiconductors (DMS) have attracted a great deal of research attention and controversy over the previous years. The initial attention was initiated by the prediction of above room temperature ferromagnetism in Mn-doped ZnO [5]. This was followed by a large number of reports of ferromagnetism in thin film transition metal (TM)-doped ZnO. However, reported values of magnetic moments and Curie temperatures were inconsistent, which led to controversy over the origin of the ferromagnetism observed at room temperature. After Dietl's prediction several groups reported the observation of room temperature ferromagnetism in TM-doped n-type ZnO-based systems. A debate is still going on whether the observed ferromagnetism is an intrinsic property of the material or a result of the formation of secondary magnetic phases due to contamination or clusters formation. From the previous published results it is clear that the sample preparation techniques and conditions are very important factors related to the presence or absence of ferromagnetism [6]. However a marvelous work has been done for Co doped ZnO system by Abhinav Pratap Singh et al. [7]. Among the transition metals, Nickel-based materials are one of the most controversial among all TM-doped ZnO, even though nickel-doped ZnO was predicted by the theoretical work of K.Sato et al. to be ferromagnetic at high temperature. Recent report on Ni doped ZnO nanorods have predicted oxygen vacancies induced

room temperature ferromagnetism for very low concentration of Ni [8]. However for Low concentrations of % Ni dopant(less than 8%) RT magnetic behavior was not observed. Similar is the case with Fe doped ZnO [9]. Some authors have reported the secondary phases or cluster formation might be responsible for the room temperature ferromagnetism and others have reported intrinsic ferromagnetism [10-13]. There is a conflict and controversy over the origin of ferromagnetism in these materials and the reported magnetic moment values [14-15]. So, clear understanding of the room temperature ferromagnetic ordering can provide us with new experimental approaches to an opportunity to develop spintronic devices. Mean field theory points out that the competition between ferromagnetic and anti-ferromagnetic exchange interaction has a strong impact on the magnetic state of the diluted magnetic semiconductors, which reveals that by changing carrier concentration i.e doping other ions into the TM –ZnO DMS has been regarded as an effective way to change the magnetic property of the original system [16-24]. In this work, we have made an attempt to achieve modified properties of ZnO based diluted magnetic semiconductor with Fe as well as Ni-Fe co-doping.

Charge (Electronics)
Ex. FET diode RAM
Spin (Magnetism)
Ex. compass, harddrive
Spintronics
spin-FET

Theoretical &Experimental Background:

- **Synthesis techniques :**
- **Solution combustion technique**

Solution Combustion Technique (SCT) or self propagating high temperature synthesis is effective energy saving method for the synthesis of a variety of advanced materials. SCT is characterized by the fact that once the initial exothermic reaction mixture is ignited by means of an external thermal sources, rapid high-temperature reaction wave propagate through the

homogeneous mixture in a self-sustained manner leading to the formation of solid material without involving any additional energy.

- **Sol-gel technique**

This technique involves the sol i.e. the colloidal solution that serves as precursor for the gel of either discrete particles or network polymers .Typical precursors are nitrates or acetates which undergo hydrolysis and poly-condensation reactions. Steps involved in the technique are:

- Preparation of homogeneous solution by either by dissolution of organic precursor in an organic solvent that is miscible with water.
- Conversion of the homogeneous solution into sol by treating with a suitable reagent (acid/base).
- Aging/Shaping
- Thermal treatment/sintering/annealing.

X-Ray Diffraction

About 95% of all solids materials can be described as crystalline. When X-Rays interact with a crystalline substance, a diffraction pattern is obtained. The X-Ray diffraction pattern of a pure substance is like a fingerprint of the substance. The powder diffraction method is used for characterization and identification of polycrystalline phases. The easy accessibility of X-ray diffraction (XRD) makes it useful method not only for the phase identification, but also for the identification of lattice structure. This technique is valid for solids or films grown on any substrate. It is useful in providing wide variety of information like the crystallinity of the material, lattice parameter, phase present and the crystallite size. The variation of the peak position with sample orientation can be utilized to collect the information. Constructive interference of the X-Ray from the successive places occurs when the path difference is an integral multiple of the wavelength so that

$$n\lambda = 2d_{hkl}\sin\theta_B$$

TEM (Transmission electron microscope)

Transmission Electron Micrograph is powerful microscopy technique where an accelerated electron beam is transmitted through a thin specimen**.** The transmission electron microscope (TEM) operates on the same principle as the light microscope but uses electrons as source instead of light. The possibility to get resolution thousand times than light microscope is maintained by electrons lower wavelength (6pm).

❖ Electrical properties

By the investigation of current and voltage relationship dc electrical conductivity can be found. Linear I-V curve behavior indicates that direct contact between the particles is the dominant conduction mechanism or otherwise it is a tunneling process. Two probe method is a powerful tool to study the electrical behavior of particles especially in nano-form.

Conductivity can be determined by the following relation:

$$\sigma = \sigma_0 \exp\left[-E_a/K_b T\right]$$

❖ Optical properties & Photo-catalytic properties

Optical properties can be studied by the Ultraviolet-Visible absorption spectroscopy. Ultraviolet-Visible absorption spectroscopy is the measurement of the intensity of the beam of light after it passes through a sample or after reflection from a sample surface. UV-Vis spectrophotometer includes transmittance, absorption and reflection measurements in UV, visible and Near Infra Red region. This technique not only provides information about the different bonding but also is an excellent tool for determining the band gap energy which is a necessary tool for determining

the conducting behaviour of semiconductors. A curve of Absorbance vs wavelength is obtained. From the Absorbance values, absorption coefficient (α) is calculated using the formula:

$$\alpha = 2.303\ A/l$$

Where A= absorbance, and l = length of light path through the sample in cm.

The UV-visible spectral data is used for the determination of optical the band gap (i.e. the difference (between the conduction band energy and the valence band) in case of various semiconductor metal oxide nanoparticles by using the Tauc relation:

$$\alpha h\nu = A\,(h\nu - E_g)^n$$

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Where, **α** is the absorption coefficient and **d** is the thickness of the sample,

E_g is the energy band gap.

n (1/2, 1, 2) is a constant is dependent on the degree of transition, **hν** is incident photon energy. The band gap is then evaluated by plotting **hν** versus $(\alpha h\nu)^2$ and extrapolating the tangent on the X-axis (Tauc Plots).

Photocatalytic studies are also required for the removal and purification of harmful dyes present in the environment as a product of industrial wastes. This property can also be studied by the use of Ultraviolet-Visible absorption spectroscopy.

❖ Magnetic measurements

Vibrating sample magnetometer is a tool for the determination of the magnetic state of sample. The VSM is based upon Faraday's law according to which an e.m.f. is induced in a conductor by a time-varying magnetic flux. In VSM, a sample magnetized by a homogenous magnetic field is vibrated sinusoidally at small fixed amplitude with respect to stationary pick-up. When a magnetic material is placed in a homogenous magnetic field, a dipole moment is induced in the

sample and is directly proportional to the product of sample susceptibility and the applied magnetic field. This sample is set to vibrate perpendicular to the uniform magnetic field by a transducer assembly and an electrical signal can be induced in suitably located pickup coils around the sample. This induced voltage, which is at the vibrating frequency, is proportional to the magnetic moment induced in the sample, amplitude of vibration and the frequency of vibration.

❖ Experimental and instrumental details

➢ Synthesis of Samples

All the samples have been prepared at Material Science Lab, H.P.U Shimla**.**

➢ Physical and structural measurements

X-rays diffraction of all samples has been done by using X-Pert PRO Diffractometer at H.P.U Shimla.

Transmission Electron Microscope has been used to analyze the surface defects and the particle size distribution by using high-resolution transmission electron microscope (HRTEM) (Jeol 2010, JEOL USA,) located at King Abdullah Institute for Nanotechnology, Riyadh Saudi Arabia.

➢ Electrical Measurements

dc conductivity has been measured by using Keithley 2611 source meter at H. P. University Shimla.

➢ UV-Visible spectroscopy measurements and Photo-catalytic properties

Experiment to study the optical properties was done on SYSTRONICS double beam spectrophotometer 2202 at Shoolini University, Solan.

➢ Raman Analysis

Raman analysis was carried out using Reinshaw at NIT Hamirpur.

- **Magnetic measurements**

The room temperature magnetization of samples has been measured by using Vibrating Sample Magnetometer ("Microsense" EV7) at H.P.University Shimla.

Magnetization with temperature has been carried out using Lakeshore' at NPL, Delhi.

Objective

From the literature survey it is found that the Fe: ZnO system is full of controversies. A lot of controversial results are there depending upon the preparation and the environment conditions. Also there is discrepancy between the theoretical and reported magnetic moment value. In order to achieve the modified properties based upon literature we attempted to achieve single phased Fe:ZnO nanosystem by two different techniques. We have also codope this system with Ni to stabilize the ferromagnetic state. Taking into account that ZnO is better photocatalyst ,we tried here to study the photo catalytic properties also.

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Plan of work done:

Synthesis of nanoparticles of

a) $Fe_xZn_{1-x}O$ (x=0.01, 0.03, 0.05) by solution combustion technique and sol-gel route.

b) $Ni_yFe_xZn_{x-y}O$ (y=0.01, x=0.01, 0.03, 0.05) by solution combustion technique.

To characterize all the samples for their Structural, Electrical Optical, Photo-catalytic and Magnetic Properties.

- X-rays diffraction: structural, lattice parameters and crystallite size of samples have been studied using x rays diffraction.

- Transmission Electron Micrograph: TEM has been used to calculate particle size confirm nano dimension of crystallites.
- Energy Dispersive X-Ray (EDAX) analysis has been used to analyze the elemental analysis of the prepared samples.

❖ Electrical properties

❖ Variation of dc electrical conductivity during heating cycle in the temperature ranges from 30-200^{0}C.

❖ Optical properties & Photo-catalytic properties

❖ UV-Visible absorption studies have been used to determine the defects as well as band gap using Tauc's equation.

❖ Raman analysis has been used to study the vibrational and rotational modes present in the samples.

❖ Photo catalytic studies have been done for dye Methylene blue.

❖ Magnetic measurements

- M-H curve at room temperature.
- Magnetization vs temperature curve.

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PROPOSED CONTENTS OF THE THESIS

Chapter 1: Introduction and review of literature.

This chapter includes introductory material required for the better understanding of diluted magnetic semiconductors and literature review which explains the need of performing this research work. At the end of this chapter aim of the research work is also mentioned.

Chapter 2: Experimental Techniques

This chapter gives a brief description of the synthesis process as well as the instrumentation of the experimental techniques which we have used in the present work. Description of the characterization techniques such as XRD, TEM, UV-Visible spectroscopy, Raman spectroscopy, VSM and I-V measurements have also been discussed.

Chapter 3: Results and Discussion

This chapter presents the results and discussions of the work that has been carried out. It includes the synthesis and characterization of all the samples prepared by both routes.

Chapter 4: Summary and Conclusion

In this chapter we summarize our work in brief and present the major conclusions drawn from the research work.

Chapter 5: Scope of Future work

This chapter includes the major suggestions for the future scope of work in this area of research.

Research papers

- **"**Structural and Mossbauer Studies of Fe Doped ZnO Nanocrystals**" Pooja Dhiman**, S. Kumar, Ashish Gautam, and M. Singh, AIP Conf. Proc. 1393, 225 **(2011).**
- "Size Controlled Synthesis and Magnetic Properties of Ni-Zn Ferrite Nanoparticles by using Aloe Vera Extract Solution" Sanjay Kumar , Ashwani Sharma, M. Singh,**Pooja Dhiman** and R.K. Kotnala, Nano Vision, Vol.1 (3), 101-114 **(2011).**
- **"**Magnetic properties of Fe doped ZnO nanosystems synthesized by solution combustion method**" Pooja Dhiman**, S.K.Sharma, M. Knobel , Ashish Gautam, and M.Singh, Research Journal of Recent Sciences, Vol. 1(8), 48-52**(2012).**
- "Structural and electrical Properties of Fe Doped ZnO Nanoparticles Synthesized by Solution Combustion Method" **Pooja Dhiman,** Ritu Rani and M.Singh, AIP Conf. Proc, 1447, 307 **(2012).**
- **"**Solution combustion preparation of Fe_2O_3-nano-flakes: Synthesis and characterization**" Pooja Dhiman**, Amit Kumar and M.Singh, Adv. Mat. Lett. **3**(4), 330 **(2012).**
- **"**Structural, Optical and Magnetic Properties of Perovskite (La1-xSrx) (Fe1-xNix) O3, (x= 0, 0.1 & 0. 2) Nanoparticles**"** Abdullah A. Saada, Wasi Khan, **Pooja Dhiman** A. H. Naqvi, M. Singh .accepted for publication in electro material letters.
- **"**Fe doped ZnO nanoparticles synthesized by solution combustion method**" Pooja Dhiman,** Khalid Mujasam Batoo, R.K.Kotnala, M.Singh, accepted for publication in micro&nanoletters.

❖ Paper presented in Conferences/Symposiums/:

- **"Structural and Mossbauer Studies of Fe Doped ZnO Nanocrystals"**International Conference on Advances in Condensed & Nano Materials held on Feb 23-26,2011at Punjab University Chandigarh.

- **"Structural and electrical Properties of Fe Doped ZnO Nanoparticles Synthesized By Solution Combustion Method",** DAE-SSPS held on dec19-23, 2011 at Chennai.

- **"Effect of In^{3+} ions on the structural, electric and dielectric properties of $Co_{0.9}Zn_{0.1}In_xFe_{(2-x)}O_4$ nanoferrite"** , International Conference on Frontiers in Nanoscience, Nanotechnology and their Applications held on feb15-16,2012 Punjab University Chandigarh.

- **"Structural and Optical Properties of Fe Doped ZnO Nanoparticles Synthesized by Solution Combustion Method"** ICWNCN-2012, held on March 13-16, 2012 at Delhi University.

- **"Synthesis and Magnetic Properties of Solution Combustion Synthesized Fe_2O_3 – Nanoparticles" ,**ECTMS -2012 ,held on March31st-2nd April, 2012 at Physics Department, Himachal Pradesh University Shimla.

- **"Effect of Fe-Ni co-doping on ZnO synthesized by Solution Combustion Method"** ISCA-2012, held on Dec7-9, 2012 at Bon Maharaj Engineering College, Mathura.

❖ Workshops Attended

- Participated in Workshop-cum Seminar on Microscopic Techniques in Nano Science held on **March 30 - April 5, 2011** at Himachal Pradesh University Shimla.
- Participated in Workshop-cum Seminar on Experimental and Computational Techniques in Material Sciences (**ECTMS-2012**) held on March31st-2nd April, 2012 at Physics Department, Himachal Pradesh University Shimla.

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